ENHANCING ACTIVITY OF IRON-BASED CATALYST SUPPORTED ON CARBON NANO PARTICLES BY ADDING NICKEL AND MOLYBDENUM

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Abstract
FeMoNi catalyst supported on carbon nanoparticles (Ketjent Black: KB) was tested in the liquefaction of sub-bituminous coals in an autoclave of 50 ml capacity. At 450^0C and 15 MPa, the liquefaction of (an Indonesian coal) Tanito Harum coal with FeMoNi/KB catalyst (10% Fe, 5% Mo, 2% Ni, 83% KB) provided oil yield as high as 77wt% that is comparable to that obtained from liquefaction with NiMo/KB catalyst (2% Ni, 10% Mo, 88% KB). The ternary catalyst was also optimized for the highest activity in terms of loading amount and order of the active components.

Keywords: coal liquefaction; iron molybdenum nickel catalysts; carbon nanoparticle support

Introduction
In fundamental research, a number of catalytic materials have been examined to find better liquefaction catalyst. However, only iron and molybdenum have been attempted in demonstration plant and so far the greatest attention has been given to Fe catalysts because of their low cost and disposability even though their activity is rather poor. To enhance the activity of iron, active metals of higher price have been combined by expecting some synergistic activation. Moreover, the very fine particles as catalyst supports having high surface area are useful to give high dispersion of active metals on its surface. In addition, as carbon support, it has a weak interaction between the metal phase and the support, which allows the quantitative conversion of the metal oxide to the active sulfide form. Thus, the carbon-supported catalysts are very effective to carry more active and costly metals at lower loading.[1]

The present authors have attempted to use the nickel-molybdenum sulfide supported on carbon nano particles (KB: Ketjen Black) to achieve excellent activity and recovery for repeated use in the liquefaction.[2] The authors also proposed FeNi sulfide on KB to reduce the cost of catalyst, which is superior to the NiMo/Al$_2$O$_3$ but inferior to the NiMo/KB.[3,4]

In the present study, catalytic activities of ternary sulfide FeNiMo/KB were examined by loading least amount of Mo on carbon nanoparticles to obtain the activity that is comparable to that of NiMo/KB catalyst. The effect of catalyst preparation method to the activity of FeMoNi/KB catalyst was also investigated.

Experimental Section
Catalyst and Materials
Fe, Ni and Mo salts were impregnated on to KB by several impregnating methods using FeC$_4$H$_2$O$_4$ (fumarate), Ni(NO$_3$)$_2$ or Ni-(Ac)$_2$, and MoO$_2$-AA in methanol and water depending on the solubility of the salts. The catalysts prepared in the present study are listed in Table 1. A prescribed amount of Ketjen black (KB) was dispersed in methanol under ultrasonic irradiation for 15 min. A mixture of iron(II) fumarate and Ni(NO$_3$)$_2$ dissolved in methanol was mixed to the KB-methanol slurry with a small amount of nitric acid (1% vol.) as an additive. The slurry had been dispersed under ultrasonic irradiation and heated at 40^0 C for 2 h before the slurry was evaporated, and dried at 120 ^{0}C for 12 h in vacuo. In the case of successive impregnation, nickel was first impregnated, being followed by iron. Other combinations of metal precursors, Mo/Ni, Fe/Mo, and Fe/Mo/Ni (the order of impregnation) were also impregnated on KB. These catalysts were presulfided by flowing 5% vol H$_2$S/H$_2$ at 360^0 C for 2 h prior to the reaction.[2,3,5]

The elemental analyses of Tanito Harum, Yilan, and Shenmu coals are summarized in Table 2. Commercially guaranteed grade tetralin (TL) was used as a liquefaction solvent, and 1-methylnapthalene was used as a reactant in the hydrogenation.
Liquefaction Procedure.

Coal liquefaction was performed in an electromagnetic-driven autoclave of 50 ml capacity. 3 g of coal, 3 g of solvent and 0.09 g of catalyst were charged to the autoclave[6]. The liquefaction was performed under 15 MPa of hydrogen pressure at 450^0C for 60 min. The heating rate to the reaction temperature was 20^0C/min, and the stirring speed was 1300 rpm.

The liquid and solid products of coal liquefaction were recovered by THF. After the THF was removed by evaporation, the product was extracted in sequence with n-hexane, acetone, and THF. The n-hexane-soluble (HS), n-hexane-insoluble but acetone-soluble (HI-ACS), acetone-insoluble but THF-soluble (ACI-THFS), and THF-insoluble (THFI) substances were defined as oil (O) and

solvent, asphaltene (A), preasphaltene (PA), and residue (R), respectively. The gas yield was calculated by the weight difference between initial coal, solvent, and recovered product. The oil yield was calculated by subtracting the initial solvent weight from the total weigh of HS. The reaction under the same conditions was repeated at least three times to make sure the experimental results that were within the errors of 1wt% daf coal base.

Hydrogenation of 1-methylnapththalene.

1-Methylnaphthalene (1-MN; 6g) and catalyst (1.5wt% based on 1-MN) were charged into a 50 ml magnetically stirred autoclave. Standard conditions for the hydrogenation were 60 min , 360°C, and 15 MPa of H_2 reaction pressure. The 1- and 5-methyltetralins and trace of tetralin were identified and quantified by GC-MS to calculate the hydrogenation activity and selectivity over the catalyst.

Results and Discussion

Effects of Ni or Mo on the catalytic activities of iron supported on KB.

Figure 1 describes yields of Tanito Harum coal liquefaction at 450°C and 15 MPa with Fe(10%) based catalyst on KB. The addition of Mo from 2 to 3% improved the oil yield of 67 and 68% , respectively, which were much higher than that of Fe(20)/KB. FeNi/KB catalyst with Ni content of 15% provided oil yield as high as 73%. More Mo or Ni content tends to increase the activity of Fe based catalyst.

Activity of the NiMo/KB catalysts with various Mo content and effects of Ni addition to the FeMo/KB catalyst

Figure 2 shows the activity of NiMo/KB catalyst with various Mo contents and the effect of Ni addition to the FeMo/KB catalyst in the liquefaction of Tanito Harum coal. The activity of NiMo/KB catalyst increased in line with the increase of Mo content in the catalyst. The Ni Mo/KB catalyst with Mo content of 10% provided a very high oil yield of 78%.

The activity of FeMo/KB catalyst was improved by the addition of Ni. Fe(10)Mo(3)Ni(3)/KB gave higher oil yield than that of Fe(10)Mo(3)/KB (see Fig. 2e and 1c). The activity was governed by Mo content of 2 to 5% that provided oil yield from 70 to 77%. It must be noted that 5% Mo in FeMoNi/KB catalyst provided a comparable oil yield to that of Ni(2)Mo(10)/KB under the same conditions. Moreover, 3 and 5% Mo in FeMoNi/KB gave oil yield of 5% higher than those of NiMo/KB with the same as Mo contents.

Effects of catalyst preparation procedure on the catalytic activity of NiMo and FeMoNi on KB

Figure 3 shows the effects of catalyst preparation procedures. For NiMo/KB catalyst, successive impregnation method appeared definitely much better than simultaneous impregnation. In impregnation procedure, molybdenum was first impregnated. However, the order of Mo/Fe/Ni in the successive method gave the same oil yield as to that in simultaneous impregnation procedure (see Figure 3c and 3d), while the order of Fe/Mo/Ni provided a slightly higher oil yield (see Figure 3e). Successive impregnation appears to give higher activity when the most dominant metal component was loaded. The reason is that the metal component is generally better dispersed in the first impregnation than in the second one because the component gets more space on the support. However, the effects in the successive impregnation may not be so strong for the component of inferior majority such as Fe.

Comparison of various catalysts in the liquefaction of Yilan and Shenmu coals

Figure 4 compares the activities of FeNi/KB, FeMoNi/KB, NiMo/KB catalysts in the liquefaction of Yilan and Shenmu coals. The activities of Fe(10)Ni(10)/KB, Fe(10)Mo(3)Ni(3)/KB, Ni(2)Mo(10)/KB catalysts in the liquefaction of Yilan coal provided 65%, 72%, and 77% oil yields, respectively. FeMoNi/KB catalyst with less Mo content gave much higher oil yields than FeNi/KB catalyst. High oil yield compensated by low gas, asphaltene, and preasphaltene yields suggests high selectivity of FeMoNi/KB catalyst. In the liquefaction of Shenmu coal (bituminous coal), the oil yield by FeMoNi/KB catalyst was higher compared to FeNi/KB in spite of lower than that of NiMo/KB catalyst.

The activity of NiMo and Fe based catalysts supported on KB in the hydrogenation of 1-methylnaphthalene

Table 3 compares the activities of catalysts in the hydrogenation of 1-methylnaphthalene at 360 °C, 15 MPa H_2, and 60 min. The Mo content governed basically the hydrogenation activity. The Mo content of 2, 3, 5, and 10% in the Fe-based and NiMo catalysts on KB provided conversions of 16, 24, 47, and 94%, respectively, regardless of the other components. The catalysts prepared by successive impregnation procedure showed a little better activity than that by simultaneous impregnation.

Conclusion

The addition of small amount of molybdenum and nickel on the iron catalyst supported on carbon nanoparticles enhances the activity of the catalyst in the liquefaction of sub-bituminous and bituminous coals. However, the hydrogenation activity for aromatic ring of the catalyst is basically influenced by Mo content. The activity of FeMoNi/KB catalyst is slightly influenced by the order of impregnation sequences in the catalyst preparation procedure.

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Table 1. Catalysts and Salts

Catalysts[a]	Fe salts	Ni salts	Mo salts
1. Fe(10)Ni(10)	$FeC_4H_2O_4$	$Ni(NO_3)_2$	-
2. Fe(10)Ni(15)	$FeC_4H_2O_4$	$Ni(NO_3)_2$	-
3. Fe(10)Mo(2)	$FeC_4H_2O_4$	-	MoO_2-AA
4. Fe(10)Mo(3)	$FeC_4H_2O_4$	-	MoO_2-AA
5. Fe(10)Mo(2)Ni(2)	$FeC_4H_2O_4$	$Ni(NO_3)_2$	MoO_2-AA
6. Fe(10)Mo(3)Ni(3)	$FeC_4H_2O_4$	$Ni(NO_3)_2$	MoO_2-AA
7. Fe(10)Mo(5)Ni(2)	$FeC_4H_2O_4$	$Ni(NO_3)_2$	MoO_2-AA
8. Ni(3)Mo(3)		$Ni-(Ac)_2$	MoO_2-AA
9. Ni(2)Mo(5)		$Ni-(Ac)_2$	MoO_2-AA
10. Ni(2)Mo(10)	-	$Ni-(Ac)_2$	MoO_2-AA

[a] Numbers in parentheses indicate the weigh percent of metals.

Table 2 Elemental Analysis of Coals Used in The Present Study

	C^a	H^a	N^a	O^a	S^a	Ash^b	H/C	O/C
Tanito Harum Coal	71.2	5.5	1.6	21.7	0.16	3.9	0.93	0.23
Yilan Coal	76.1	5.6	1.3	16.7	0.22	3.8	0.88	0.167
Shenmu Coal	78.8	5.1	1.1	14.7	0.21	3.9	0.78	0.14

[a] in Wt % (d.a.f.)

[b] Wt.% in

Table 3 Hydrogenation of 1- Methylnapthalene [a]

Catalysts	Conversion % [b]
Fe(10)Ni(10)/KB (simultaneous impregnation)	14
Fe(10)Ni(10)/KB (successive impregnation)	16
Fe(10)Mo(2)Ni(2)/KB (simultaneous impregnation)	16
Fe(10)Mo(3)Ni(3)/KB (simultaneous impregnation)	24
Fe(10)Mo(3)Ni(3)/KB (successive impregnation)	28
Fe(10)Mo(5)Ni(2)/KB (successive impregnation)	47
Ni(2)Mo(10)/KB (simultaneous impregnation)	94
Ni(2)Mo(10)/KB (successive impregnation)	98

[a] Catalysts, 0.09 gr; 1-methylnapthalene, 6 g

[b] Reaction conditions : 360 ^{0}C; 15 MPa; 60 min; stirring speed : 1300 rpm.
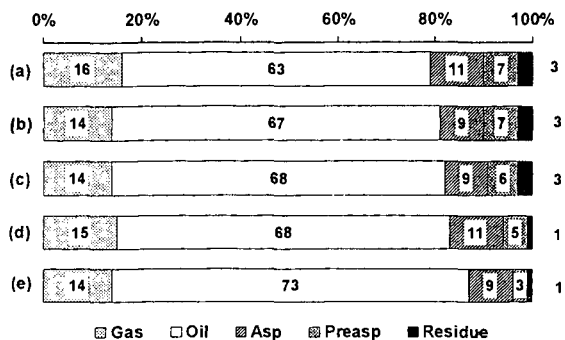
Figure 1. Effect of Ni or Mo addition to the Fe(10)/KB on the liquefaction of Tanito Harum coal : (a) Fe(20)/KB; (b) Fe(10)Mo(2)/KB; (c) Fe(10)Mo(3)/KB; (d) Fe(10)Ni(10)/KB, (e) Fe(10)Ni(15)/KB.
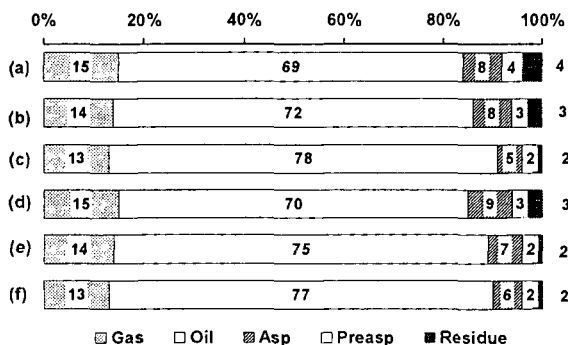

Figure 2. Activity of the NiMo/KB catalysts with variable Mo content and Effect of addition of Ni to the FeMo/KB catalysts on the liquefaction of Tanito Harum coal : (a)Ni(3)Mo(3)/KB; (b) Ni(2)Mo(5)/KB; (c) Ni(2)Mo(10)/KB; (d) Fe(10)Mo(2)Ni(2)/KB; (e) Fe(10)Mo(3)Ni(3)/KB; (f) Fe(10)Mo(5)Ni(2)/KB.
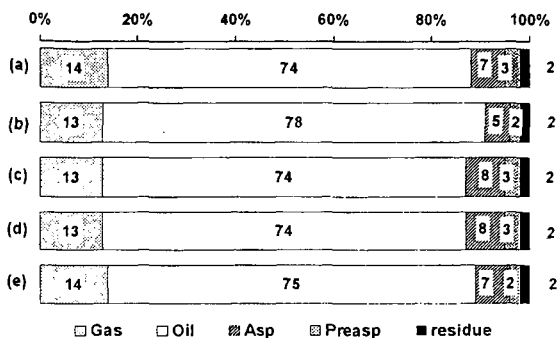
Figure 3 Effect of preparation method on the catalytic activity of Mo-based catalysts in the liquefaction of Tanito harum coal : (a) Ni(2)Mo(10) simultaneous impregnation process; (b) Ni(2)Mo(10) successive impregnation process; (c) Fe(10)Mo(3)Ni(3) simultaneous impregnation; (d) Fe(10)Mo(3)Ni(3) successive impregnation process I* , (e) Fe(10)Mo(3)Ni(3) successive impregnation process II**.

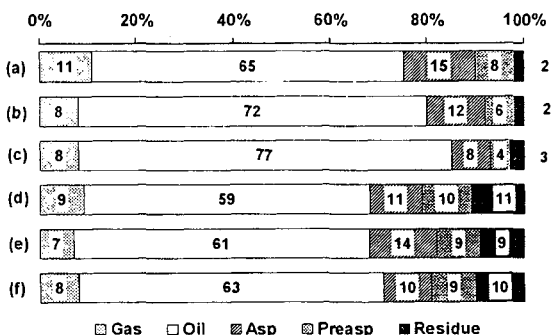* Mo was firstly impregnated

** Fe was firstly impregnated

Figure 4 Activities of Fe(10)Ni(10)/KB, Fe(10)Mo(3)Ni(3)/KB, and Ni(2)M0(10)/KB catalyst in the liquefaction of Yilan, and Shenmu coals with tetralin solvent. (a), (b), (c) Yilan coal; (d), (e), (f) Shenmu coal; (a), (d), Fe(10)Ni(10)/KB catalyst, (b), (e) Fe(10)Mo(3)Ni(3)/KB catalyst; (c), (f) Ni(2)M0(10)/KB catalyst.